BOULDER 2003 SUMMER SCHOOL: FRONTIERS IN MAGNETISM

MICROSCOPIC BASIS OF MAGNETISM

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Sub title:

MAGNETISM OF INSULATORS, METALS AND THINGS-IN-BETWEEN

INSULATORS

- Hydrogenic Atoms . Review of 3d-- transition metal atoms
  Hunds Rule, Spin orbit X^ion

- Hydrogen molecule H_2: Heitler London vs. Mulliken/Bands
  Determinants
  Onsite U, exchange J overlap ≡ bonding ≡ A.E.M.

- Array of H atoms or Si P— Mott's problem
  Long Ranged Coulomb — Mott's original problem
  Short Ranged " — Mott-Hubbard problem
  t/U expansion in insulators — Mott vs Slater view

- Crystal Field splittings - overlap - Superexchange & Direct Exchange

  - Examples of C-F splittings
  - Anderson's superexchange vs. Charge Transfer Insulators
    Jump to
  - Goodenough - Kanamori - Anderson rules and their origin

- Double exchange: Manganates, Zener - Anderson - Hasegawa.

- Small things: Spin orbit X^ion and its consequences
  Single ion terms, Dzyaloshinsky-Moriya
  g-factors

• § Hydrogenic atoms: quick review:

$$H = \sum \frac{p_i^2}{2m} + \sum_i V(r_i) + e^2 \sum_{i<j} \frac{1}{|r_i - r_j|}$$
$$- g\mu_B \sum \vec{S}_i \cdot \vec{H} - \mu_B \sum \vec{L}_i \cdot \vec{H}$$
$$+ \frac{\hbar}{2m^2c^2} \sum \vec{S}_i \cdot \left\{ \vec{\nabla} V(\vec{r}_i) \times \vec{p}_i \right\} + g^2\mu_B^2 \sum \left\{ \frac{\vec{S}_i \cdot \vec{S}_j}{r_{ij}^3} - \frac{3 \vec{S}_i \cdot \vec{r}_{ij} \; \vec{S}_j \cdot \vec{r}_{ij}}{r_{ij}^5} \right\}$$

Here $V(r_i) = -\frac{Ze^2}{|\vec{r}_i|}$ is Bare coulomb $\times$'ion

This is a formal $1/c$ expansion since $\mu_B = \frac{e\hbar}{2mc}$.

$$\vec{\nabla} V(\vec{r}_i) = \frac{\vec{r}_i}{|\vec{r}_i|} V'(r_i) \quad \therefore \quad \text{last/1st term} = \frac{\hbar Z e^2}{2m^2c^2} \sum_i \frac{1}{|r_{ij}|^3} \vec{S}_i \cdot \vec{L}_i$$

$\vec{L}_i = \vec{r}_i \times \vec{p}_i$.

$$= \sum \zeta(r_i) \vec{S}_i \vec{L}_i \cdot$$

$$\boxed{\zeta(r_i) > 0}$$

•§§

This is too hard a many body problem - we use Hartree Fock orbitals to define effective one body problem:

$$V_{HF}(r_i) = V(r_i) + V_{Hartree} - V_{Fock}^{exch} \qquad [\psi_i^{\alpha}]$$

Classical Bohr radius $r_n^{Bohr} = a_0 n^2/Z$; $a_0 = \frac{\hbar^2}{me^2} = .52 A^\circ$

$\langle r_{n\ell} \rangle = (3n-\ell)(3n-\ell+1) \frac{r_n^{Bohr}}{2}$ $\sim 25 A^\circ$ Cu $n=3$ $\ell=2$ 29

$\sim 15 A^\circ$ O_2 $n=2$ $\ell=1$ 16

$Z \to Z - \sigma \equiv Z_{eff}$. σ = screening.

§§ Spin orbit parameter

$$\overline{\zeta(r_i)} = \frac{\hbar Z e^2}{2m^2c^2} \left\langle \frac{1}{r_i^3} \right\rangle \qquad \therefore \int r_i^2 |\psi|^2 \zeta(r_i) \simeq \frac{Z^2}{c^2} - \overline{\zeta}$$

$H_{SO} \simeq \lambda \sum \vec{L}_i \cdot \vec{S}_i \qquad \lambda > 0 \qquad \sim Z^2$ ∴ quite appreciable for large Z.

Au ~ largest S-O among metals

$\lambda \sim 1000\,°K$ to $1000\,°k$

↑ Trans metals ↳ Rare earths

§§ Magnetism mostly about unfilled shells - 3-d T-M
4-d T-M
4-f Lanthanides
5-f Actinides.

Cu^{2+}

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
[Ar]	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$
Val.	3^+	2^+ 3^+ 4^+	2^+ 3^+ 4^+ 5^+	2^+ 3^+ 5^+ 6^+	2^+ 3^+ 4^+ 7^+	2^+ 3^+	2^+ 3^+ 4^+	2^+ 3^+	1^+ 2^+

§§ Unfilled shells and Hund's rule:

(i) S_{Tot} maximized
"~~EE~~ J effect"

(ii) L maximized
"U effect"

$\uparrow\uparrow$ $\quad S = 1, L = 3$

$\uparrow\uparrow\uparrow\uparrow$ or $\uparrow\uparrow\uparrow\downarrow$

$^3F_{(3/2,3)}$ ✓ or $(3/2,2)$

J effect ⇒ orthogonal orbitals have F, M, J i.e. prefer // spins. U ⇒ repulsion effect minimized by L spread

(iii) $\lambda > 0$ for $n <$ half $\therefore |\vec{L}-\vec{S}| = \vec{J}$

$\lambda < 0$ for $n >$ half $\therefore \vec{L}+\vec{S} = \vec{J}$

$V = \lambda \sum_{i=1}^{n} \vec{l}_i \cdot \vec{s}_i$ $\underline{\underline{\lambda > 0}}$ originally

If $n > 0$ half filling add and subtract $\vec{l}_i \cdot \vec{s}_i$

$7 + 3 - 3$ $\therefore$ Filled shell $- \lambda \Sigma \vec{l}_i \cdot \vec{s}_i$

But Filled shell → inert $\therefore V_> = -\lambda \Sigma \vec{l}_i \cdot \vec{s}_i$ (holes)

$V_< = \lambda \Sigma \vec{l}_i \cdot \vec{s}_i$ (e^-)

$\vec{s}_i = \frac{\vec{S}}{n}$ (wigner eckart Th.)

$\therefore V_> = -\lambda \vec{L} \cdot \vec{S}$ & $V_< = \lambda \vec{L} \cdot \vec{S}$ $\therefore$ 3rd rule of Hund's

If Degeneracy lifting by external fields ~ e.g. electric fields

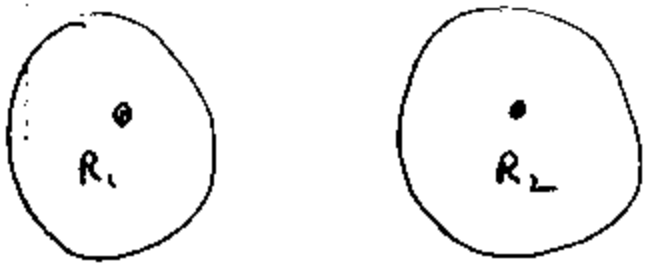
This is the basis of Crystal field effects – later.

$\psi_{n,l,m,\sigma} = R_{nl}(|r|)\, Y_{lm}(\hat{\Omega})\, \chi_\sigma$

$E = E_n$ Bohr atom $= -\pi^2 \frac{e^2 z}{2(Ro)}$

In reality due to X^{ions} $E_{n,l}$ i.e. l dependence too

§ Origin of Exchange: The H_2 molecule:



$$H = \frac{p_1^2+p_2^2}{2m} - \frac{e^2}{|r_1-R_1|} - \frac{e^2}{|r_1-R_2|} - \frac{e^2}{|r_2-R_1|} - \frac{e^2}{|r_2-R_2|} + \frac{e^2}{|r_1-r_2|}$$

$$\psi(r_1\sigma_1, r_2\sigma_2) = -\psi(r_2\sigma_2, r_1\sigma_1)$$

$\chi_\Sigma(\sigma) = \alpha$ or β (spin-part).

N=2 very special ψ factors into spin ⊗ space

$= \phi(r_1, r_2)\ \chi(\sigma_1, \sigma_2)$

sym — a-sym

a-sym — sym

Spin: Triplet = symmetric $\alpha_1\alpha_2$, $\beta_1\beta_2$, $\frac{\alpha_1\beta_2+\beta_1\alpha_2}{\sqrt{2}}$

singlet = a-sym $\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}$

H does not explicitly depend on spin-variables and yet we claim:

$H_{eff} = C + J\,\vec{S}_1\cdot\vec{S}_2$ $\qquad$ $\boxed{E_S - E_t = -J}$

- Space part insoluble — Variational

Heitler London — vs — Mulliken molecular orbital

non-polar state — polar state

ϕ_t = antisym (sp. part) ϕ_s = symm-space part

H-L choose two intuitively "good" states

$\phi_{1s}(r-R_1)$ and $\phi_{1s}(r-R_2)$ 1-S Hydrogenic states

$$\phi^{s}_{t}(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \frac{\phi_{1s}(r_1-R_1)\,\phi_{1s}(r_1-R_2) \mp \phi_{1s}(r_1-R_2)\,\phi_{1s}(r_2-R_1)}{(1 \mp \Delta^2)^{1/2}} \right\}$$

Δ = overlap $= \int \phi_{1s}(r_1-R_1)\,\phi_{1s}(r_1-R_2)\,dr_1$

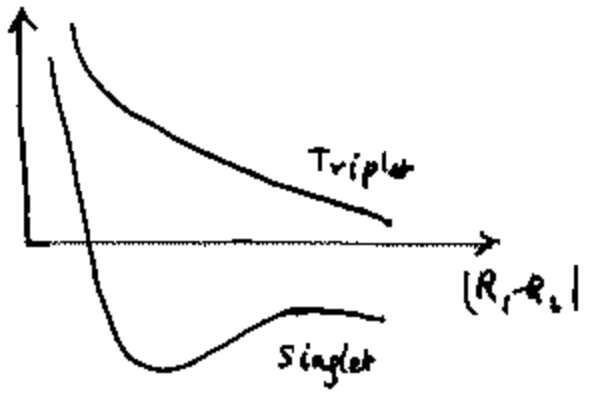
$\sim e^{-|\vec{R}_1-\vec{R}_2|/a_0}$

$$\mathcal{E}^{t}_{s} = 2\mathcal{E}_0 + \frac{1}{(1 \mp \Delta^2)} \{ A \mp B \}$$

$$\mathcal{E}_s - \mathcal{E}_t = \frac{2}{(1-\Delta^4)} \{ B - \Delta^2 A \}$$

$$B = \int \phi(r_1-R_1)\,\phi(r_1-R_2)\,\phi(r_2-R_1)\,\phi(r_2-R_2) \left\{ \frac{e^2}{|r_1-r_2|} - \frac{e^2}{|r_1-R_2|} - \frac{e^2}{|r_2-R_1|} \right\}$$

$$A = \int \phi^2(r_1-R_1)\,\phi^2(r_2-R_2) \left\{ \frac{e^2}{|r_1-r_2|} - \frac{e^2}{|r_1-R_2|} - \frac{e^2}{|r_2-R_1|} \right\}$$



E-diff is determined largely by B term. $\varepsilon_s < \varepsilon_t$ if $B < 0$

$$B = \int \mu(r_1)\,\mu(r_2)\,K(r_1 - r_2) \qquad \mu \text{ is a non-positive fn: } \phi(r_1 - R_1)\,\phi(r_1 - R_2)$$

If $K = \dfrac{e^2}{|r_1 - r_2|}$ only, i.e. pure coulomb, it is

pos definite :: $B > 0$ $\left\{ B = \langle \mu\mu | K | \mu\mu \rangle = \sum_\lambda |K\mu(\lambda)|^2 k_\lambda \geq 0 \right\}$

∴ For B to become -ve need overlap!

$$B = \int \mu(r_1)\mu(r_2)\,\frac{e^2}{|r_1 - r_2|} - 2\Delta \int \frac{e^2}{|r_1 - R_2|}\,\phi(r_1 - R_1)\,\phi(r_1 - R_2)$$

∴ Adage:

no overlap (orthogonal orbitals)	$\Rightarrow$ F.M. $\varepsilon^t < \varepsilon^s$
overlap	$\Rightarrow$ A-F.M $\varepsilon_s < \varepsilon_t$

$J \sim$ .1 ev High T_c 1000°K
$\sim$ .01 ev 100°K
.001 ev 10°K
} all these are realized

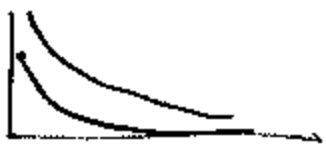
• Mulliken – M-O theory

$$\phi_{\pm}(r) = \left\{ \phi_{1s}(r-R_1) \pm \phi_{1s}(r-R_2) \right\} \frac{1}{2\sqrt{1 \pm \Delta}}$$

$$\phi_{sym}(r_1, r_2) = \phi_+(r_1)\,\phi_+(r_2) \quad \text{or} \quad \phi_-(r_1)\,\phi_-(r_2)$$

$$\phi_{asym}(r_1, r_2) = \left\{ \phi_+(r_1)\,\phi_-(r_2) - \phi_+(r_2)\,\phi_-(r_1) \right\} \frac{1}{\sqrt{2}}$$

Here we find no binding!



Essential difference:

M-O theory contains polar states –

e.g. ~ $\phi_{1s}(r_1 - R_1)\,\phi_{1s}(r_2 - R_1)$ → Very costly – Due to Coulomb rep.

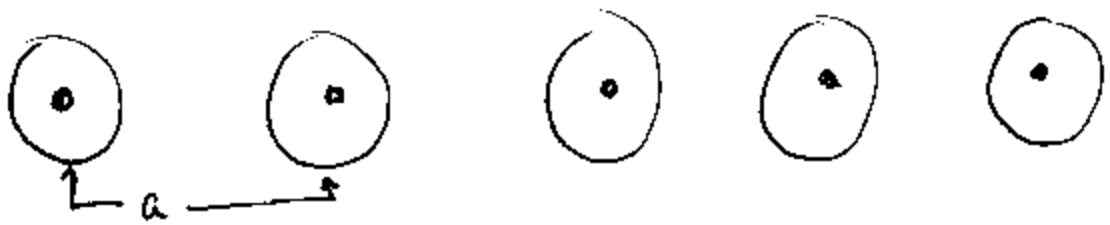
H-L never has polar states.

But H-L cannot carry a current — { Primitive Insulator

M-O can! — { Primitive Metal

§. Array of H atoms, Mott's problem:

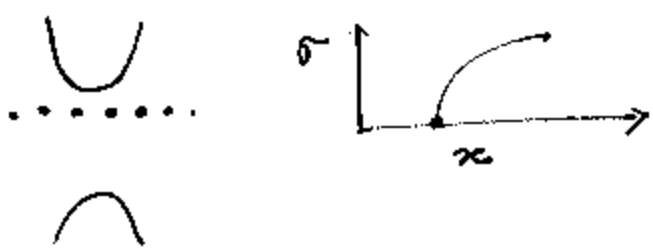
Mott 1947



When $a \gg a_0$ expect isolated atom behaviour - insulator ~ essentially distinguishable e^-s

For $a \sim a_0$ orbitals "crunch" into each other - expect metallic behaviour. ∴ Expect transition as a varies.

⊙ Shallow Donor states in Si: P. very popular '60's ftr



Many complications in real systems
- multi valley
- Anderson Disorder
- M-A Transition

⊙ Perhaps Quantum dot arrays can be designed to realize Mott's

We can again approach problem from H-L or Band point of view. ⊙ Need suitable 1-e^- functions.

$\phi_{1s}(r - R_n)$ is highly inconvenient, so we can form Wannier fns from these in two steps

Step ①:

$$\phi_k(r) = \gamma \sum_n \phi_{1s}(r - R_n)\, e^{ik(r-R_n)}$$ P.B.C's

$k = \frac{2\pi}{L}\{\text{int}, \text{int}, \text{int}\}$ γ = normalizn

ϕ_{1s} is a "natural" atomic state

$(\phi_k, \phi_{k'}) = \delta_{k,k'}$, $\phi_k(r + R_j) = e^{i\vec{k}\cdot R_j}\phi_k(r)$

Step ②:

$$W(r - R_n) = \frac{1}{\sqrt{N}} \sum_{k_j} e^{-ik_j(r_i - R_n)}\, \phi_{k_j}(r_i)$$

we'll call these as $W_n(r)$ and express it in the basis of $W_n(r)$:

$$\psi_\sigma(r) \cong \sum_n W_n(r)\, C_{n\sigma}$$ { strictly $W_n^\alpha(r) C_{n\sigma}^\alpha$, α = Band index →

{ Projection to a 1 Band model!

Examples:

Program: search for (low energy) effective Hamiltonians!

KE $\int \psi_\sigma^\dagger(r) \left[\frac{p^2}{2m} + V(r) \right] \psi_\sigma(r)$

$$\sim \varepsilon_0 \sum c_{n\sigma}^\dagger c_{n\sigma} - \frac{1}{2} \sum_{ij}{}' t_{ij} c_{i\sigma}^\dagger c_{j\sigma}$$

$$\begin{cases} t_{ij} = \int w^*(r - R_i) \left\{ p^2/2m + V(r) \right\} w(r - R_j) \\ \varepsilon_0 \equiv t_{ii} \end{cases}$$

P.E. $= \frac{1}{2} \int \psi_{\sigma_1}^\dagger(r_1) \psi_{\sigma_2}^\dagger(r_2) \frac{e^2}{|r_1 - r_2|} \psi_{\sigma_2}(r_2) \psi_{\sigma_1}(r_1)$

$$\simeq \frac{1}{2} \sum V_{ij,kl} \, c_{i\sigma_1}^\dagger c_{j\sigma_2}^\dagger c_{k\sigma_2} c_{l\sigma_1}$$

$$V_{ijkl} = \int w(r_1 - R_i) \, w(r_2 - R_j) \, w(r_2 - R_k) \, w(r_1 - R_l) \frac{e^2}{|r_1 - r_2|} \, dr_1 dr_2$$

This is still too much detail (irrelevant?)

Mott: $\sim \frac{1}{2} \sum V_{ij,ji} \, c_{i\sigma_1}^\dagger c_{j\sigma_2}^\dagger c_{j\sigma_2} c_{i\sigma_1}$

$$V_{ij,ji} = U[i-j] \sim \frac{e^2}{|R_i - R_j| \, \kappa}$$

κ = dielectric constant {interband effects} w fns ~ ck

Anderson 1950, 57 }
Hubbard: 1962 }

$$\mathcal{H} \sim \frac{1}{2} \sum V_{ii,ii} \, c_{i\sigma_1}^\dagger c_{i\sigma_2}^\dagger c_{i\sigma_2} c_{i\sigma_1}$$

$$= \frac{U}{2} \sum n_{i\sigma_1} n_{i\sigma_2} ,$$

$$U = \begin{cases} \\ \\ \\ \end{cases} \int w^2(r_1 - R_i)\, w^2(r_2 - R_j)\, \frac{e^2}{|r_1 - R_2|}$$

1 ev
~ 5 ev
10 ev

using $(n_{i\sigma})^2 = n_{i\sigma}$, rewrite

$$V_{int} = U \sum n_{i\uparrow} n_{i\downarrow} + \text{constant}$$

Motti: $\quad c_{k\sigma} = \frac{1}{\sqrt{N}} \sum e^{-i\vec{k}\cdot\vec{r}_i} c_{i\sigma}$

$$\mathcal{H} = \sum \epsilon_k c^+_{k\sigma} c_{k\sigma} + \frac{1}{2} \sum v_q c^+_{k+q\sigma} c_{k\sigma} c^+_{p-q\sigma'} c_{p\sigma'}$$

$$v_q = \frac{4\pi e^2}{\kappa q^2} \qquad \{\text{correct for small } q\}$$

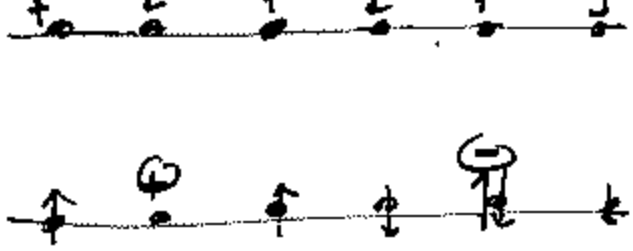
Metallic state ∃ for high enough density or small enough a –

Metallic state characterized by screening

$$\kappa \to \kappa_q = \left(1 + \frac{q_{TF}^2}{q^2}\right)\kappa_0 \qquad q_{TF}^2 = \frac{4me^2}{\hbar^2 \kappa_0} n^{1/3}$$

$$v_q^{eff} = \frac{4\pi e^2}{\kappa_0 (q^2 + q_{TF}^2)} \sim \frac{e}{|r_{ij}|} e^{-|r_{ij}| q_{TF}} \frac{4\pi e^2}{\kappa_0}$$

Screened Coulomb – Yukawa



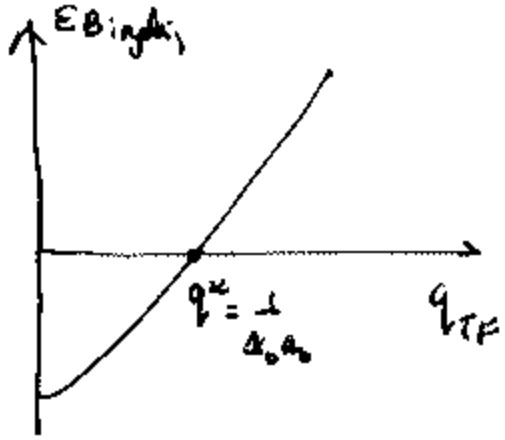
1 $\bar{e}$/atom $a \gg a_0$

In absence of screening: e Coulomb has ∞ # bound states

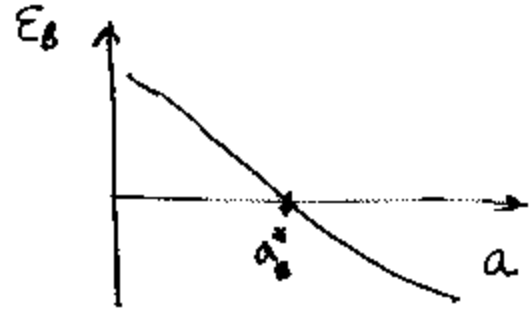
$\therefore$ Hole & doublon will form a bound molecule – (Mott Exciton)

$\therefore$ Self-consistent insulating state

If screening is nonzero and big enough, (i.e. $q_{TF} > q^*$)
Yukawa potential has no bound states (3-d)



But $q_{TF} \sim \frac{1}{\sqrt{a}}$



$$a^* \simeq \kappa_0 a_0$$

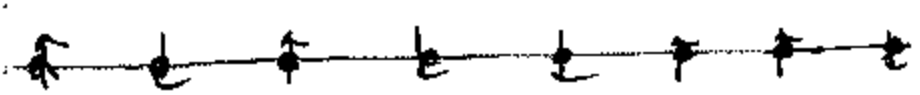
$\therefore$ Metallic state inconsistent for $a < a^*$.
For $a > a^*$ instability – (Mott Excitonic Instability)
$\therefore$ Jump to insulator
1st order Transition

So Hubbard-Anderson limit:

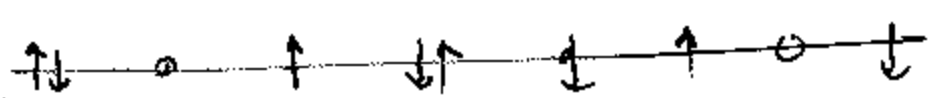
Examine insulating state stability

$$H = U \sum n_{i\uparrow} n_{i\downarrow} - \sum t_{ij} c_{i\sigma}^{+} c_{j\sigma}$$

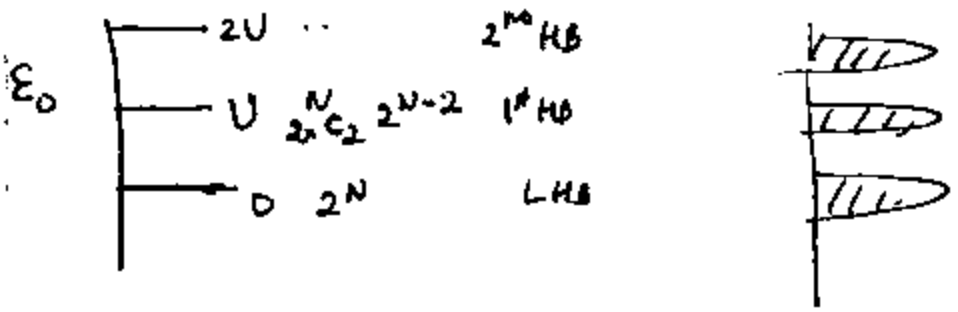
H_0 $\quad$ $H_1 \equiv V$ $\quad$ 1 e⁻/atom



2^N fold deg.
$\varepsilon = 0$

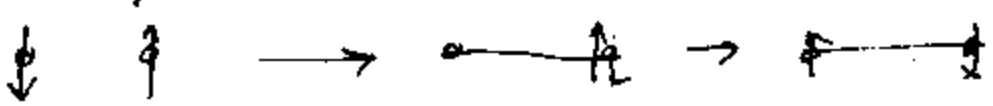


$= 2U$



qualitative lifting of degeneracy

In pictures



LHB $\quad$ UHB $\quad$ LHB

$|\Phi_N\rangle$ = state in LHB

$|\chi_n\rangle$ = " " 1st UHB

LHB $\quad$ Lexical order and spin order!

$c_a^{+} c_b^{+} c_d^{+} |V\rangle \rightarrow$ ok

$c_a^{+} c_d^{+} c_b^{+} |V\rangle \rightarrow - c_a^{+} c_b^{+} c_d^{+} |V\rangle$

$c_\uparrow^{+} c_\downarrow^{+}$ ok

$c_\downarrow^{+} c_\uparrow^{+} \rightarrow - c_\uparrow^{+} c_\downarrow^{+}$

$|\varphi_n\rangle$ ~example $c^+_{1\uparrow} c^+_{2\downarrow} c^+_{3\downarrow} c^+_{4\uparrow} \cdots c^+_{N\downarrow} |0\rangle$

since 1 2 3 — N are redundant. it can be specified by $|\sigma_1 \cdots \sigma_N\rangle$ $\sigma_j = \uparrow$ or $\downarrow$

$H = H_0 + V$ V is 1st order in t

$$|\psi\rangle = \sum c_n |\varphi_n\rangle + \sum d_n^{t} |\chi_n\rangle + \sum f_n^{t^2} |\gamma_n\rangle$$

$$(H_0 + V)|\psi\rangle = (E_0 + \tilde{E}_1)|\psi\rangle \qquad \tilde{E}_1 = \varepsilon_1 + \varepsilon_2^{2nd}$$

$\sim$

$\sum c_n (H_0 - \varepsilon_0)|\varphi_n\rangle = 0$ ~~$\varepsilon_1 \sum c_n |\varphi_n\rangle$~~ — $\leftarrow t^0$

$\leftarrow t^1$

$$\sum d_n (H_0 - \varepsilon_0)|\chi_n\rangle + \sum c_n V|\varphi_n\rangle = \varepsilon_1 \sum c_n |\varphi_n\rangle$$

But $\langle \varphi_n | V | \varphi_n \rangle = 0 \quad \therefore \varepsilon_1 = 0$

$$d_n = -\sum_m \frac{c_m \langle \chi_n | V | \varphi_m \rangle}{U}$$

$O(t^2)$

$$\varepsilon_2 \sum c_n |\varphi_n\rangle = \sum f_n (H_0 - \varepsilon_0)|\gamma_n\rangle + \sum d_n V|\chi_n\rangle$$

$\langle \varphi_n |$ But $\langle \varphi_n | \gamma_n \rangle = 0$

$$\varepsilon_2 c_n = \sum_m d_m \langle n | V | \chi_m \rangle = -\frac{1}{U} \sum c_e \langle n|V|\chi_m\rangle\langle \chi_m | V | \varphi_e \rangle$$

∴ Effective Low energy Hamiltonian

$$H^{eff}_{n,m} = -\frac{1}{U}\sum_{j}\langle \varphi_n | V | \chi_j \rangle \langle \chi_j | V | \varphi_m \rangle$$

$|\chi_j\rangle$ is a 1st UHB state with 1 "doublon"

$$V = -\sum t_{ij}\, c^{+}_{i\sigma} c_{j\sigma}$$

$$\cdot V : V \cdot = -\sum t_{ij} \cdot c^{+}_{i\sigma_1} c_{j\sigma_1} : c^{+}_{l\sigma_2} c_{m\sigma_2} \cdot t_{lm}$$

$$= -\sum \left(t_{ij} t_{ji}\right) \cdot c^{+}_{i\sigma_1} c_{j\sigma_1} : c^{+}_{j\sigma_2} c_{i\sigma_2} \cdot$$

Excercise:

$$\cdot c^{+}_{i\sigma_1} c_{j\sigma_1} : c^{+}_{j\sigma_2} c_{i\sigma_2} \cdot = \left(\frac{1}{2} - 2\vec{S}_i \cdot \vec{S}_j\right)$$

∴

$$H_{eff} = +\frac{1}{U}\sum_{ij} t^2_{ij}\left(2\vec{S}_i \cdot \vec{S}_j - \frac{1}{2}\right)$$

$$= \frac{4}{U}\sum_{i<j} t^2_{ij}\left(\vec{S}_i \cdot \vec{S}_j - \frac{1}{4}\right)$$

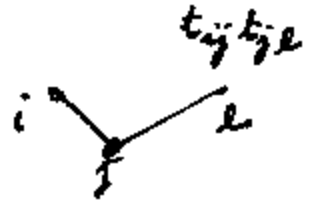
Note: If V^2 cannot connect & V^3 can - need to push one more level. $H_{eff} \sim t^3/(\Delta E)^2$

• Note: In case V connects in 1st nbrs itself -
{ Less than ½ filling }

$$H = H_J + (-t) \sum t_{ij} c_{i\sigma}^{+} c_{j\sigma}$$

Almost correct — 2nd order term picks up a correction also

$$H_J = \sum_{ij} \frac{2}{U} t_{ij}^2 \left\{ \vec{S}_i \cdot \vec{S}_j - \frac{1}{4} n_i n_j \right\} \quad + \frac{1}{U} \sum c_{i\sigma_1}^{+} c_{j\sigma_1} c_{i\sigma_2}^{+} c_{e\sigma_2}$$

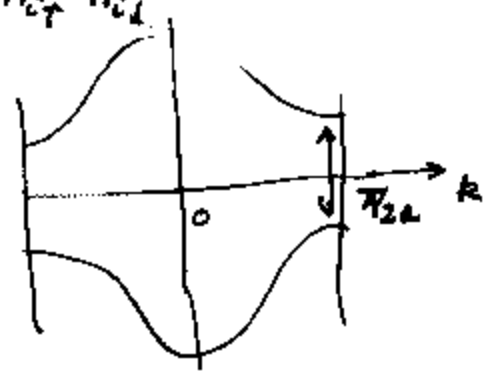


§ Slater's split band AF state { SDW of Overhauser .. }

At ½ filling an insulating state emerges if we break translation invariance

$$H = - \sum t_{ij} c_{i\sigma}^{+} c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow}$$

$$\overline{n_{i\sigma}} = \frac{\rho}{2} \pm (-1)^i \frac{m}{2}$$



Gap vanishes as $m \to 0$

∴ Above T_N ~ again a metal

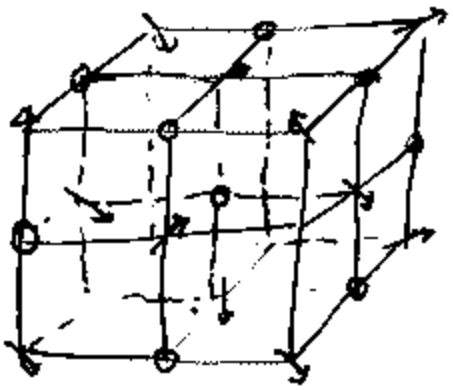
∴ Slater's insulator differs fundamentally from Mott's. Mott's insulator need not have LRO —

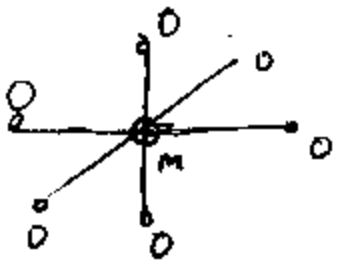
However ⇒ Split Band AFM has magnons of scale that (if LRO ∃) $\to \frac{4t^2}{U}$ for $U >> t$.

§ Superexchange - CF splittings - Transition Metal oxides
- Direct Exchange (M-M)

H.A. Kramers, P.W. Anderson, Goodenough, Kanamori -

NaCl structure & Rocksalt :



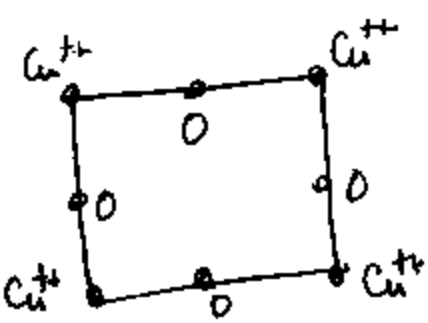


$M^{++}O^{--}$

M	Ti	V	Cr	Mn	Fe	Co	Ni	CuO
	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
Metal/Ins	Metal	Met/Ins		Ins	Ins	Ins	Ins	
AFM/F	Pauli	~		AFM	AFM	AFM	AFM	
T_N				122°	198	293°	523°K	

M - O - M structure.

La_2CuO_4 :

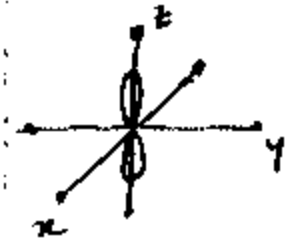


J_N 1000°K
AFM

Crystal field splitting:

d^1 $\{Ti^{3+}$ or $Cu^{2+}\}$ in Octahedral Environment

5 fold degeneracy lifted in intuitively clear way

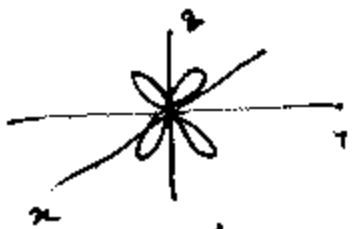


$d_{3z^2-r^2}$

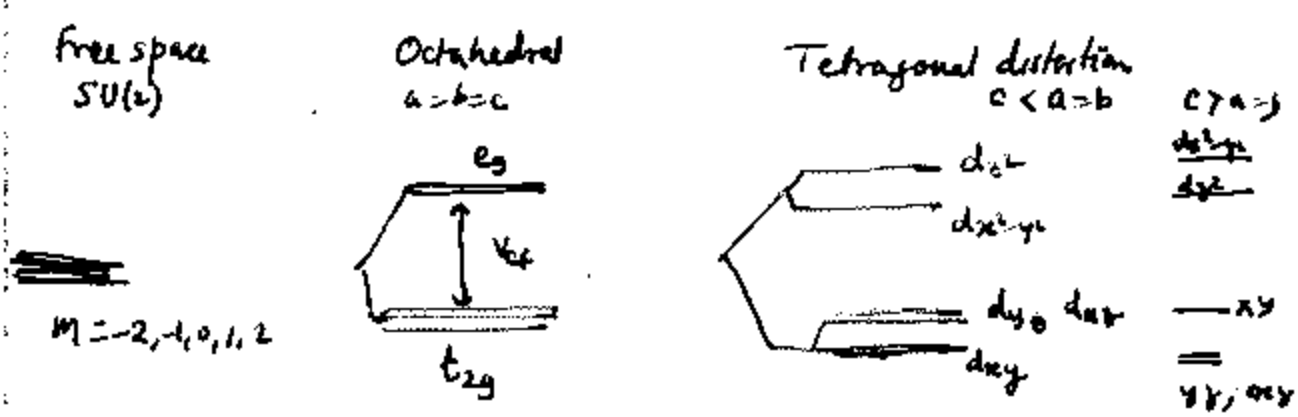
$d_{x^2-y^2}$

d_{xy}

d_{xz}



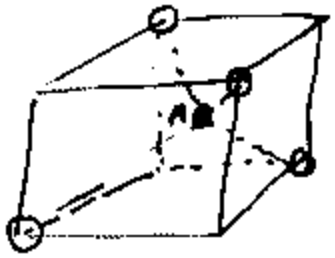
d_{yz}



Crudely speaking $V_{Cf}(r) = \sum_{n \in \text{next shell}} V(r - R_n)$

In metals it is less meaningful - these orbitals overlap from bands - often broader than V_{Cf}!

Tetrahedral env: inversion



Here the d_{xy} d_{xz} d_{yz} orbits extend more towards O^{--} ∴ are higher in energy.

$$d_{x^2-y^2} = (Y_2 + Y_{-2})\frac{1}{\sqrt{2}} \qquad d_{z^2} = Y_0$$

$$d_{xy} = (Y_2 - Y_{-2})\frac{1}{\sqrt{2}} \qquad \left.\begin{aligned} d_{xz} &= Y_1 + Y_{-1} \\ d_{yz} &= Y_1 - Y_{-1} \end{aligned}\right\}$$

If λ, J_{Hund}, U, V_{CF} are all operative in a solid.
∴ d^2 d^3 d^4 d^5.. are more involved

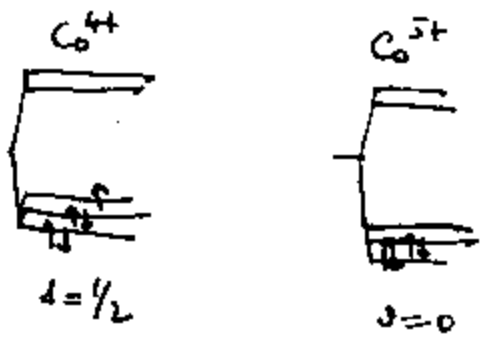
- Quenching of $\vec{L}$
  - Wide variety of behaviour seen

some simple → Mn^{2+} : d^5 : $S = 5/2$ $L = 0$

Some Complex – Re-do Na_xCoO_2 Co^{4+} - Co^{3+} Δ^x lattice:

Co has low-spin behaviour:

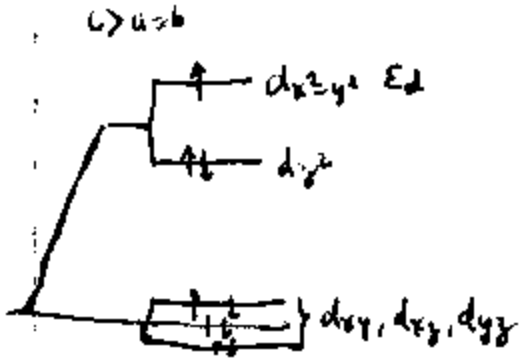
Clearly $J_H < V_{CF}$

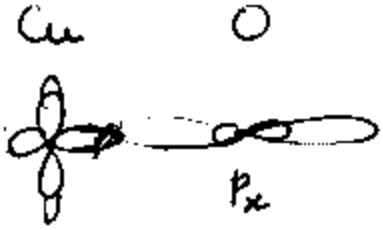


J Kanamori Pros Theor Phys 17 177 (57)
J Phys Chem Solids 10 87 (1959)

§ La_2CuO_4 Super exchange vs. charge transfer pt of view

Cu^{++} d^9 in tetragonal environment





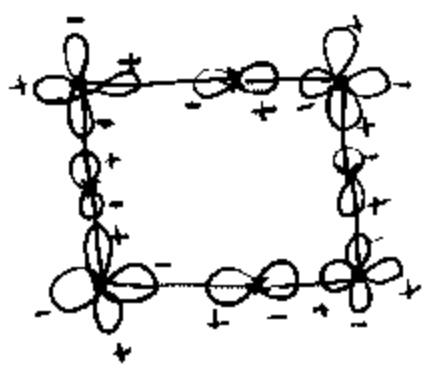
Convert to hole picture:

$\varepsilon_p > \varepsilon_d$ in the

$-\varepsilon_p$

$U_{dd} = \infty$

ε_d Cu Oxygen Cu



$$H = -V_{p-d}\sum c^{+}_{j\sigma} p_{j\sigma} + U_{pp}\sum n_{p_i\uparrow} n_{p_i\downarrow}$$

$$+ U_{dd}\sum n_{d_i\uparrow} n_{d_i\downarrow}$$

$$+ \varepsilon_p \sum \left(p^{\dagger}_{j_x} p^{x}_{j} + p^{\dagger}_{j_y} p^{y}_{j} \right) + \varepsilon_d \sum c^{+}_{j\sigma} c_{j\sigma}$$

Anderson's superexchange view point

First forget U's & form bands

— — → Both bands, non bonding, Antibond, Bonding Band

$V_{pd}=0$ levels

1 hole/Cu

∴ Effectively 1 Band model at ½ filling. Rewrite in wannier basis – back to Hubbard model & t-J

Wannier states are "sophisticated"

Charge transfer pt of view — G. Sawatzky J Allen PRL 53 2339

{ B.E.S spectroscopy gives locations of core levels
X.P.S Bremsstrahlung - isochromat - spectroscopy

$\hbar\omega$

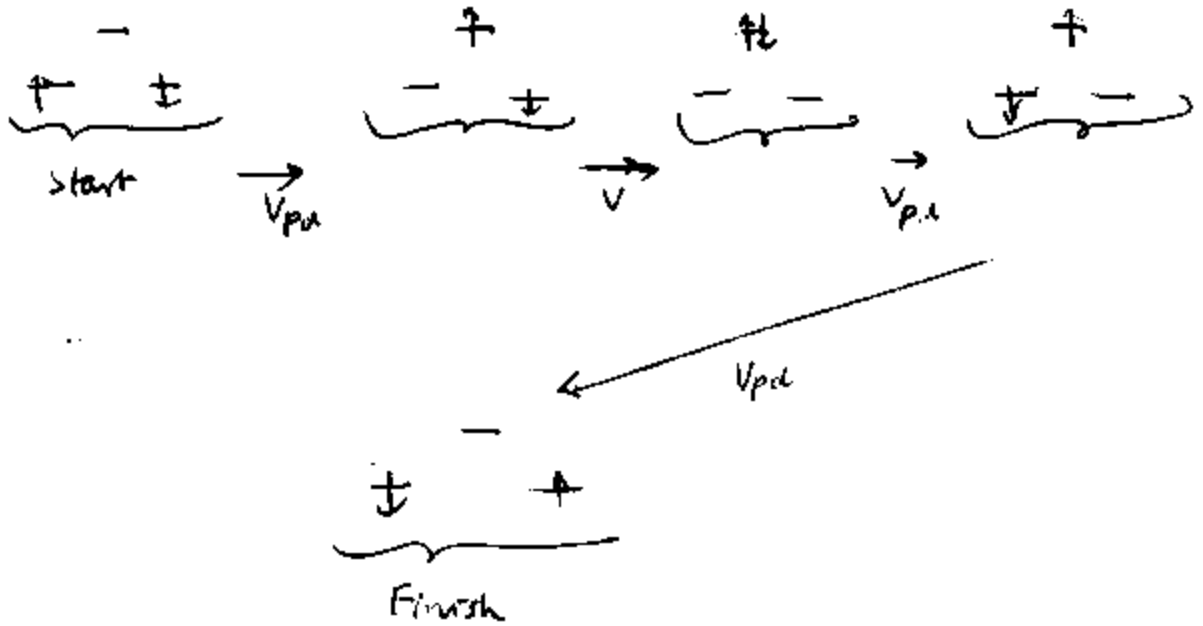
$\hbar\omega \geq \varepsilon_{core}$ – Knock out by X-ray photons & watch energy δ e's

— ε_p

Gap is not U but $(\varepsilon_p - \varepsilon_d)$

↑ ↓ S_i → $J_{ex} \sum_{\langle ij \rangle} \left(\vec{S}_i \cdot \vec{S}_j + \frac{1}{4} \right)$

$J_{ex} = \frac{32\, V_{pd}^4}{(\varepsilon_p - \varepsilon_d)^3}$ 4th order process



∴ It is a distinction without an essential difference at ½ filling

Does make a difference on doping – not simple t-J model

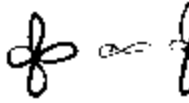
S.S. PRL 63 1288 (1989)

ℒ Goodenough – Kanamori – Anderson rules on strength & sign of J

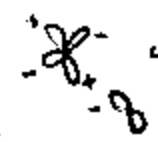
(A) • 180° Bonds – Strongly AFM

$d_{z^2} - p - d_{z^2}$

e_g – bonds

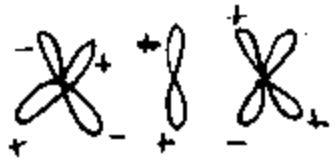


(a) ⌊ 90° Bonds $Mn F_2$ 102° AFM



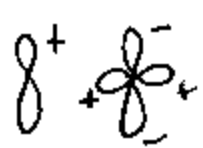
(B) t_{2g} bonds 180° — weak AFM

Cr^{3+}:



(C) Orthogonal orbitals – FM $La_2 Fe Cr O_6$ Terakura PRB 64 104402 (2001)

eg $\begin{cases} d_5 - d_3 \\ M_n - V \end{cases}$

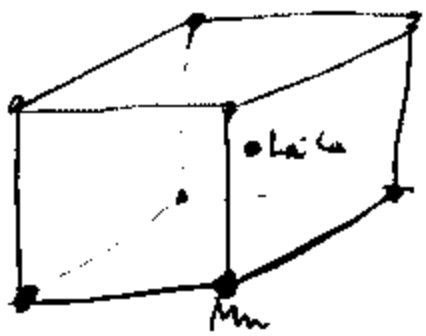


§ Double exchange

Zener, Anderson-Hasegawa

$La^{3+} Mn^{3+} O_3^{6-} \longrightarrow La^{3+}_{1-x} Ca^{2+}_{x} Mn^{3+}_{1-x} Mn^{4+}_{x} O_3^{6-}$

Perovskite



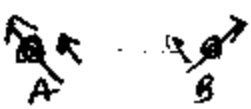
O on face centers

Mn^{3+} d^4 $\quad$ Mn^{4+} d^3

$\uparrow\uparrow\uparrow\uparrow$ $\quad$ $\uparrow\uparrow\uparrow$

Core forms $S = 3/2$ in both &
Mn^{3+} has extra e^- that can hop.

Consider 2 site problem



$$\mathcal{H}_{2\text{-}s} = -\sum_{\sigma} t\left(c^{+}_{1\sigma} c_{2\sigma} + c^{+}_{2\sigma} c_{1\sigma}\right) - J\left(\vec{S}_1 \cdot \vec{S}_A + \vec{S}_2 \cdot \vec{S}_B\right)$$

J is from Hund's rule and is >0. If $J<0$ the argument still works provided $t \neq 0$ on both sites.

Main point: $\vec{S}_1$ & $\vec{S}_B$ are fairly large: semiclassical. e^- that hops — does so conserving spin $\Rightarrow$ prefers $S_A \parallel S_B$

It cannot hop if $\vec{S}_A$ anti parallel to $\vec{S}_B$

∴ F-M good AFM → bad

we need to construct e^- spinors for local $\hat{z}$ axis along some $\hat{\eta} \equiv (\theta, \phi)$

$$\chi_{+,\hat{\eta}} = \begin{bmatrix} \cos\theta/2 \; e^{i\phi/2} \\ \sin\theta/2 \; e^{-i\phi/2} \end{bmatrix} \quad \& \quad \chi_{-,\hat{\eta}} = \begin{bmatrix} -\sin\theta/2 \; e^{i\phi/2} \\ \cos\theta/2 \; e^{-i\phi/2} \end{bmatrix}$$

$$\chi^{\dagger}_{\sigma,\hat{\eta}} \cdot \chi_{\sigma',\hat{\eta}} = \delta_{\sigma,\sigma'} \qquad \langle \vec{S} \rangle_{\pm} = \pm \tfrac{1}{2} \hat{\eta} \Big\} \text{ easy to check}$$

The hopping $\sum_{\sigma} C^{+}_{1\sigma} C_{2\sigma}$ is a spin scalar

∴ can also be written as $\sum_{\sigma} C^{+}_{1,\hat{\eta},\sigma} C_{2,\hat{\eta},\sigma}$

where $C_{1,\hat{\eta},\sigma} = \sum_{\sigma'} \chi_{\sigma',\hat{\eta}} C_{1\sigma'}$

∴ we need to do a simple semiclassical calc!

Freeze $\vec{S}_A$ and $\vec{S}_B$ along two directions. Think of $J \gg t$

$$\langle \downarrow | T | \downarrow \rangle = t \; \chi^{\dagger}_{+,\hat{\eta}_B} \cdot \chi_{+,\hat{\eta}_A} = t \Big\{ \cos\tfrac{\phi_1}{2} \cos\tfrac{\phi_2}{2} \cos\tfrac{\theta_1 - \theta_2}{2} + i \sin\tfrac{(\phi_1 - \phi_2)}{2} \cos\tfrac{(\theta_1 + \theta_2)}{2} \Big\}$$

$$= |t_{eff}| e^{i\Psi}$$

Ψ is $= 2 \tan^{-1} \left\{ \tan\tfrac{\phi_2 - \phi_1}{2} \; \dfrac{\cos\left(\frac{\theta_1 + \theta_2}{2}\right)}{\cos\left(\frac{\theta_1 - \theta_2}{2}\right)} \right\}$ Effective Peierls phase factor!

$|\langle \uparrow | T | \downarrow \rangle| = |t_{eff}| = +|t| \cos\left(\frac{\theta_{12}}{2}\right)$

∴ Energy of hopping prefers $\theta_{12} \sim 0$

↑ ↑ ↗ ↗ → → → → → →

Layers 1 2 3 4 5 . . . . .

$$E = -zt\,x\,N \cos\frac{\theta}{2} + N J_s z S^2 \cos\theta$$

↑ superexchange

z = # neighbours in interlayer terms..

x = # Ca ions / # Cu

Minimize

$\cos\frac{\theta_0}{2} = \frac{tx}{4 J_s S^2}$ changes with x

C-M-R - industrial scale effort - other lectures.

∫ SMALL THINGS MATTER:

A typical Hamiltonian looks like -

$$\mathcal{H} = \frac{1}{2}\sum_{ij} J_{ij}\,\vec{S}_i \vec{S}_j$$

$$- g\mu_B \Sigma \vec{S}_i \cdot \vec{H}$$

$$+ D_s \Sigma (S_i^z)^2 + \sum_{\langle ij \rangle} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j)$$

$$+ g^2\mu_B^2 \sum_{i<j} \left\{ \frac{\vec{S}_i \cdot \vec{S}_j}{|r_{ij}|^3} - \frac{3(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{|r_{ij}|^5} \right\}$$

$\mu_B = \frac{e\hbar}{}$

Two "culprits" – dipole-dipole
spin-orbit coupling

(a) Dipole-Dipole x'ion

In purely cubic systems, if J is very small – interesting and novel physics – $Gd_2Ti_2O_7$ our pyrochore as an example
Usually J is very big or lattice distorts

$\langle\ \rangle \rightarrow -D S_z^2$ type for MnF_2 from intersite x'ln

$\langle\ \rangle$ — $-(\vec{L}\cdot\vec{S})^2$ on one site
$+ \beta(S_z^2)^2$ β – diff to estimate

(b) Spin-orbit coupling
$\lambda \vec{L}\cdot\vec{S}$ $\lambda \sim O(1/c^2)$

(I) Influence on g factor – uniaxial systems $C > a = b$

Again Cu^{2+} $\uparrow$ $d_{x^2-y^2}$ ε_1 ϕ_1
$\downarrow$ d_{3z^2} ε_2 ϕ_2

$\#$ | ε_2, more

Single site
$H = +\lambda \vec{L}\cdot\vec{S} - \mu_B \vec{H}\cdot(\vec{L}+\vec{S})$

In absence of λ we have 2 states $\phi_1 \chi_\sigma \quad \sigma = \pm 1$.

Perturbation in λ yields a spin orbit doublet (Kramer's theorem)

$$\Psi_\pm = \phi_\pm \chi_\pm + \sum_{\nu \sigma'} \frac{1}{\varepsilon_1 - \varepsilon_\nu} \phi_\nu \chi_{\sigma'} \langle \phi_\nu \chi_{\sigma'} | \lambda \vec{L} \cdot \vec{s} | \phi_\pm \chi_\pm \rangle$$

Depending on ν, we can find non vanishing matrix elements

$\Psi_\pm$ are not "pure spin projection".

$$\vec{H} = H(\sin\theta, 0, \cos\theta)$$

$\langle \Psi_\pm | \mathcal{H}_{Zeeman} | \Psi_\mp \rangle$ is 2×2 matrix

$$\cos\theta\, \mu_B H \begin{bmatrix} -\cos\theta & \sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} + \mu_B H \lambda \begin{bmatrix} -\frac{\lambda_4}{\varepsilon_3 - \varepsilon_1}\cos\theta & -\frac{\lambda}{\varepsilon_4 - \varepsilon_1}\sin\theta \\ \frac{-\lambda}{\varepsilon_4 - \varepsilon_1}\sin\theta & \frac{\lambda_4}{\varepsilon_3 - \varepsilon_1}\cos\theta \end{bmatrix}$$

$$\varepsilon = \pm \frac{\mu_B H}{2} \sqrt{g_\perp^2 \sin^2\theta + g_\parallel^2 \cos^2\theta}$$

$$g_\perp = 2\left\{1 + \frac{\lambda}{\varepsilon_4 - \varepsilon_1}\right\} \qquad g_\parallel = 2\left\{1 + \frac{4\lambda}{\varepsilon_3 - \varepsilon_1}\right\}$$

$$\therefore \frac{\Delta g}{g} \sim \lambda$$

§ Dzyaloshinski - Moriya

A B

$$\mathcal{H} = + \lambda \left(\vec{L}_a \cdot \vec{S}_a + \vec{L}_b \cdot \vec{S}_b \right) - t_{ab} \left(c^+_{a\sigma} c_{b\sigma} + c^+_{b\sigma} c_{a\sigma} \right)$$

$$+ U \cdot \Big\{ \mathcal{H}_{SL} = 2 \sum_i \left(\vec{\nabla}(V(r)) \times \vec{P}_i \right) \cdot \vec{S}_i$$

we transform to Kramers doublets at a and b

$$\Psi_{\pm} = \Phi_{\pm} \chi_{\pm} + \lambda \Phi_m \chi_{\pm} + \lambda \Phi_m \chi_{\mp}$$

$\downarrow c$

$$\therefore T = - \left(t^{\uparrow\uparrow}_{ab} c^+_{a\uparrow} c_{b\uparrow} + t^{\uparrow\downarrow}_{ab} c^+_{a\uparrow} c_{b\downarrow} + t^{\downarrow\uparrow}_{ab} c^+_{a\downarrow} c_{b\uparrow} + t^{\downarrow\downarrow}_{ab} c^+_{a\downarrow} c_{b\downarrow} \right)$$
$$+ h.c + U \sum (n_{a\uparrow} n_{a\downarrow} + n_{b\uparrow} n_{b\downarrow})$$

$$- t^{\sigma_1 \sigma_2}_{ab} = \int \psi^+_{a\sigma_1} \left\{ \mathcal{H}_0 + g \mathcal{H}_1 \right\} \psi_{b\sigma_2} \qquad g \sim \lambda$$

$$t_{ab} = \tfrac{1}{2} \left(t^{\uparrow\uparrow}_{ab} + t^{\downarrow\downarrow}_{ab} \right) \quad C^z_{ab} = \tfrac{1}{2} \left(t^{\uparrow\uparrow}_{ab} - t^{\downarrow\downarrow}_{ab} \right)$$

$$C^+_{ab} = t^{+-}_{ab} \quad C^-_{ab} = t^{-+}_{ab}$$

$C^{\pm}$ C^z are pure imaginary (L is imaginary operator & hatt or real!)

$$\mathcal{H} = \overbrace{-t_{ab} \sum c^+_{a\sigma} c_{b\sigma}}^{T_0} + \overbrace{\vec{C}_{ab} \cdot \sum_{\sigma_1} c^+_{a\sigma_1} \vec{\tau}_{\sigma_1 \sigma_2} c_{b\sigma_2}}^{T_1} + h.c + U n_\uparrow n_\downarrow$$

$$\mathcal{H}_{eff} = -\frac{1}{U} \cdot (T_0 + T_1) : (T_0 + T_1) \cdot$$

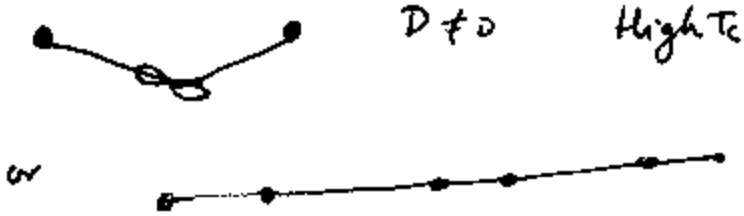
$$= \mathcal{H}_{Hees} - \frac{1}{U} \{ \cdot T_0 : T_1 \cdot + \cdot T_1 : T_0 \cdot \} \quad + O(\lambda^2)$$

$$= \mathcal{H}_{Kin.} + \mathcal{H}_{DM}$$

$$\mathcal{H}_{DM} = \frac{4i}{U} \sum_{\langle ij \rangle} \left(t_{ab} \vec{C}_{ab} - t_{ba} \vec{C}_{ba} \right) \cdot \vec{S}_a \times \vec{S}_b$$

$$= \sum_{\langle ij \rangle} \vec{D}_{ab} \cdot \vec{S}_a \times \vec{S}_b$$

- $D_{ab} = 0$ if $\exists$ inversion point between a & b



Dimerized systems w/ spin gap. $CuGeO_3$.

$$\frac{D}{J} \sim \left(\frac{\Delta g}{g} \right)$$

This is experimentally a good rule of thumb!

- $\vec{D}$ direction

D lies in mirror plane if one $\exists$